Investigation of the Fiber Reinforcement of a Cobalt Base Alloy for Application at Elevated Temperature

May 1966

Prepared under Contract NASW-1365

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ABSTRACT

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A technique was developed for incorporating alumina and silicon carbide fibers in Haynes alloy 36, a cobalt base alloy. Alumina or silicon carbide fibers plunged into carbon rich Haynes alloy 36 were found in solidified cast test specimens. A definite increase in tensile strength at 1500° F was noted with increasing amounts of ceramic fibers in carbon rich Haynes alloy 36. Difficulties in consistently identifying alumina and silicon carbide whiskers in Haynes alloy 36 by standard metallographic techniques were encountered.

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I. INTRODUCTION

There currently exists a demand for materials capable of operating in extreme high temperature environments under applied stress. Typical of the problems encountered for elevated temperature application is the turbine engine. Operating efficiency is dependent upon operating temperature, and any increase in the operating temperature of the turbine blades has a significant effect on engine performance.

Cobalt base alloys are available for use under stress at temperatures up to 2000°F, but currently it is difficult to obtain strength levels in these alloys which meet all of the necessary requirements. Research is presently being performed to improve or develop cobalt base alloys with superior properties. Dispersion strengthening by powder metallurgy techniques in conjunction with coatings for oxidation resistance are two major research areas of current interest. Recently, with the advent of fiber reinforcement of metal alloys, researchers feel that this technique exhibits great potential for increasing the strength of metals. A variety of fiber reinforced metal alloy systems employing alumina, silicon carbide, boron and graphite fibers have been investigated on a laboratory scale, and the results obtained using these fibers to reinforce metal matrices has been encouraging, but many problems still exist.

These problems include wetting of the fiber by a molten metal matrix, prevention of chemical attack of the fiber by the molten matirx, differences in the thermal expansion of the fiber and matrix, density differences which would effect fiber distribution in a molten matrix and a variety of other

problems related to the particular systems under investigation. Although these problems exist, for some systems they have been overcome, and successful fiber reinforced materials have been fabricated. The fabrication of fiber reinforced materials has been limited primarily to powder metallurgical techniques and liquid metal infiltration of fiber mats. Neither of these techniques is practical for producing large complicated shapes.

MITRON has demonstrated that fiber reinforced metals can be cast to shape and applications for patents have been filed. The technique developed by MITRON consists of introducing the fibers into the molten metal, stirring to distribute the fibers in the melt, and then pouring the fiber containing metal into the necessary mold to obtain the desired casting. This system has been utilized to introduce fibers into several metal alloys, but to-date concentration of effort has been on the aluminum alloys. Alumina and silicon carbide fibers have been dispersed into melts of aluminum - 4.5% copper alloy, stirred and the melts poured into graphite molds. The as-cast metallographic structure reveals fibers in the eutectic areas extending into the primary grains. Figures 1 and 2 are 3 micron diameter silicon carbide fibers in the as-cast structure. Figure 3 illustrates the fibers in a partially solutionized structure. Figure 4 and 5 are 10-30 micron diameter alumina fibers in the as-cast structure. Figures 6 illustrates the fibers in a completely solutionized structure.

Based on the above noted experiments it was reasonable to suggest the possible application of this technique to casting fiber reinforced cobalt base alloys for application at high temperature. The use of fiber reinforced cobalt base alloys appeared to offer an attractive solution to improving the

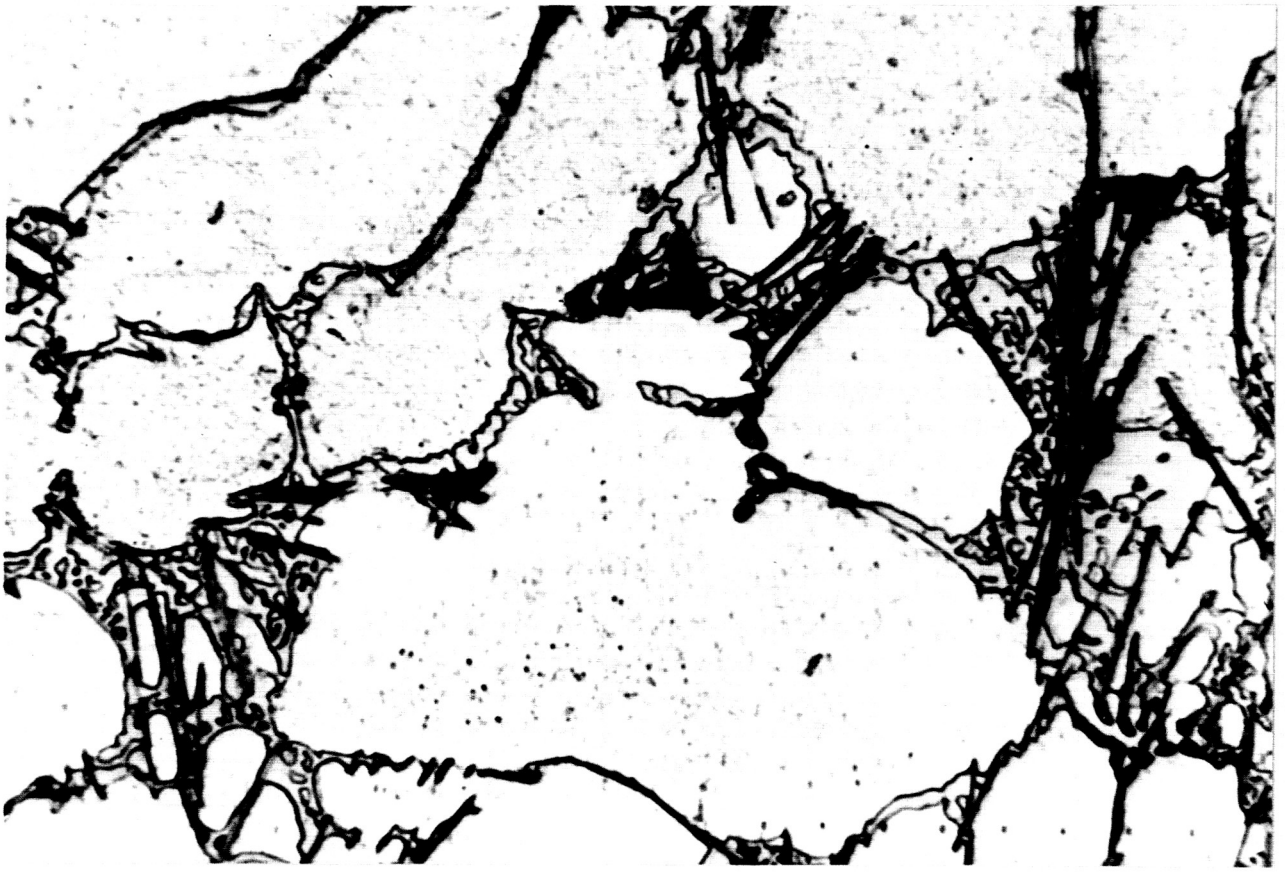

Figure 1 - Microstructure of experimental copper-aluminum alloy as-cast in machined graphite molds. Note the appearance of 3.0 micron diameter silicon carbide fibers at the grain boundaries.
Keller's Etch

800X

Figure 2 - Microstructure of experimental copper-aluminum alloy as-cast in machined graphite molds. Note the appearance of 3.0 micron diameter silicon carbide fibers at the grain boundaries.
Keller's Etch 800X

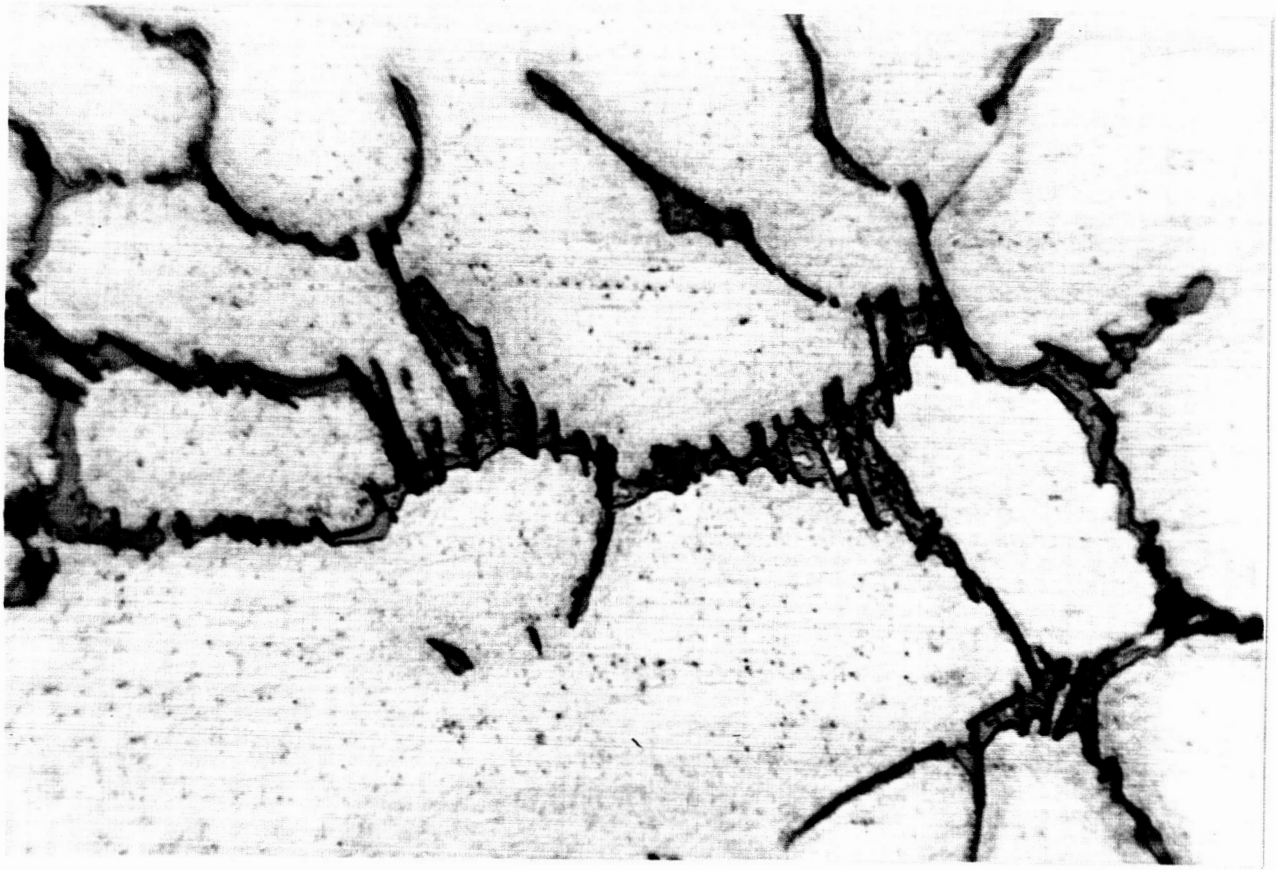

Figure 3 - Microstructure of experimental copper-aluminum alloy, Solutionized one hour at 990°F, water quenched. Note appearance of 3.0 micron diameter silicon carbide fibers at prior grain boundaries
Keller's Etch

800X

Figure 4 - Microstructure of experimental copper-aluminum alloy as-cast in machined graphite molds. Note appearance of 10-30 micron diameter aluminum oxide fibers at the grain boundaries
Keller's Etch 800X

Figure 5 - Microstructure of experimental copper-aluminum alloy as-cast in machined graphite molds. Note appearance of 10-30 micron diameter aluminum oxide fibers at the grain boundaries
Keller's etch 800X

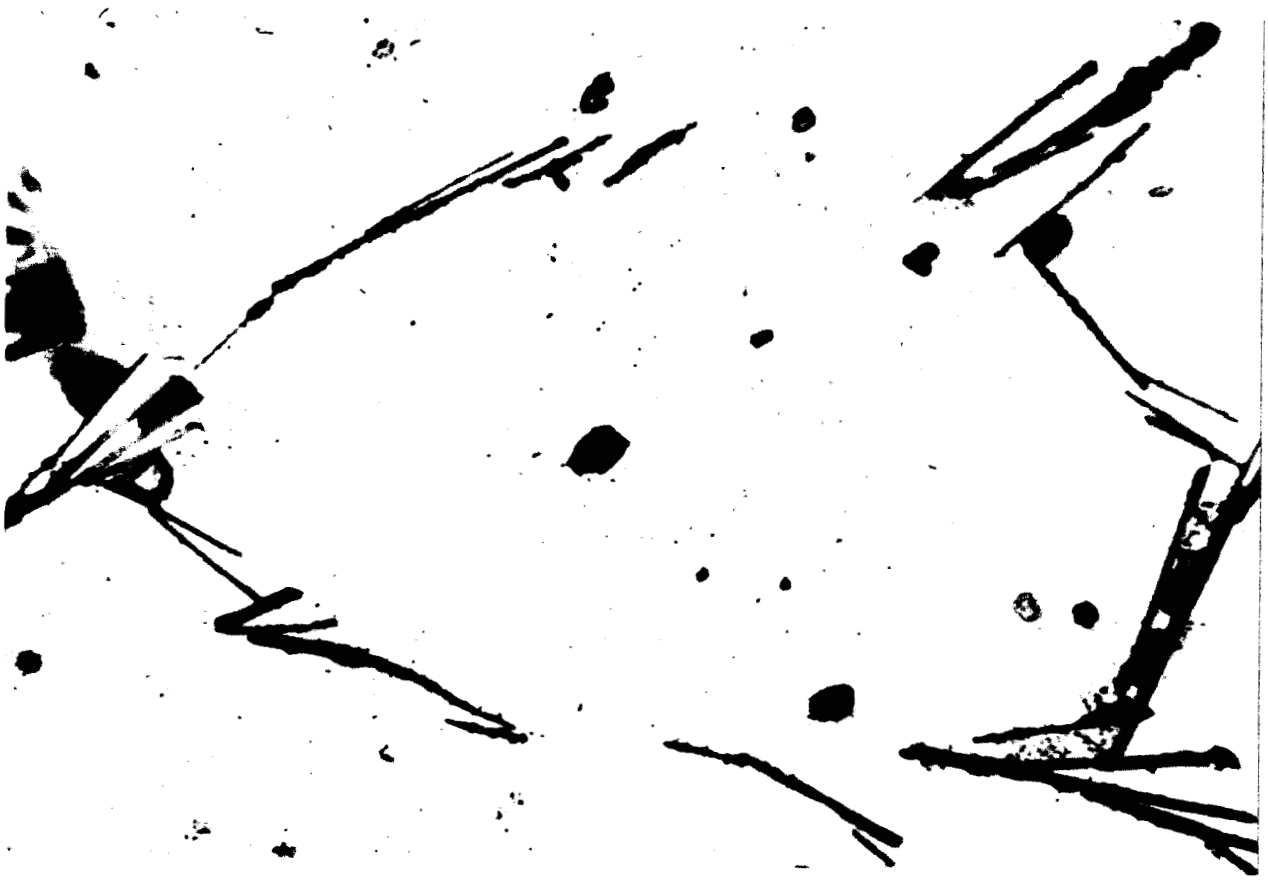

Figure 6 - Microstructure of experimental copper-aluminum alloy, solutionized one hour at 900°F, water quenched. Note appearance of 10-30 micron diameter aluminum oxide fibers at prior grain boundaries
Keller's Etch 800X

useful temperature range of these materials. The strengthening mechanism of the cobalt base alloys is related to the intermetallic compounds which are formed. These are complex carbides of the M_7C_3, M_6C and $M_{23}C_6$ type and are thought to block or retard the movement of dislocations by acting as dispersoids. The introduction of fibers to form a super strength network joining the carbides would act to further retard dislocation movements, slip and plastic flow. The high strength of the cobalt base alloys at elevated temperatures is also believed to be associated with the dissolution of carbides increasing the solid solution strength of the matrix. This strength might be increased even further by transferral of the stress to the fiber with the result being an increase in the usable temperature range of the alloys.

Many research programs have demonstrated that various fibers are chemically attacked by a molten matrix, but this effect is not necessarily deleterious, provided it is limited to the fiber surface. In many cases the interaction zone between the fiber and matrix forms a bond which results in adequate stress transferral from the matrix to the fiber. If the rate of reaction is not rapid, and the fibers are not exposed to the molten matrix for extended periods of time, the reaction would be limited and would not impair the fiber's properties. Based upon the excellent results in reinforcing cast aluminum alloys with ceramic fibers at MITRON and the excellent potential of fiber reinforcement for improving elevated temperature properties, a program to reinforce Haynes alloy 36 with alumina and silicon carbide fibers was proposed and initiated.

II. EXPERIMENTAL PROGRAM

The object of this program was to develop techniques for incorporating alumina and silicon carbide fibers into melts of Haynes alloy 36, study the distribution of the fibers in the matrix and determine the wetting characteristics of the fiber and matrix. In the event the fibers were not compatible with the matrix, various techniques to improve wettability between the fiber and the matrix were to be attempted. The proposed techniques included the use of fluxes as wetting agents, coating of fibers, and variations in alloy composition to establish a compatible system. After establishing the proper reinforcement techniques, the as-cast mechanical properties of fiber reinforced composites were to be determined at elevated temperature.

In the initial work, five (5) lb heats of Haynes alloy 36 shot were melted in a magnesia crucible using a 20 kw induction unit. The crucible was covered and an inert argon atmosphere was used to protect the melts. Alumina and silicon carbide fibers were used for this investigation. The chemical analysis of the Haynes alloy 36 and a description of the fibers used for this investigation are given in Table I.

Heat 1. Five (5) pounds of alloy 36 were melted and poured into 5 button molds. These castings were used to establish a method for introducing the fibers, determine the effect of the molten metal on the fibers and establish a metallographic technique for identifying fibers in the alloy 36 matrix. A small quantity of alumina fibers was wrapped in aluminum foil and placed in mold 1. Molten metal was poured into this mold but the fibers and aluminum foil floated to the surface. A small quantity of alumina fibers was placed in mold 2. Molten metal was poured into this mold and the fibers floated to the surface before the metal solidified. An attempt was made to introduce fibers into the metal stream during pouring. This failed because the fibers,

TABLE I

Chemical Analysis - Haynes Alloy 36

Cr	18.67	Si	0.68
N	15.27	Ni	9.96
Fe	1.05	Mn	1.04
C	0.39	B	.025

Co - Balance

Properties of Al_2O_3 and SiC Fibers

Al_2O_3 (type 2B)	-	Thermokinetic Fibers Inc.
diameter	-	1 to 10 microns
length	-	75 to 1250 microns
SiC (type DS)	-	Carborundum
diameter	-	0.5 to 3 microns
length	-	10 to 300 microns

which were wrapped in aluminum foil, hit the side of the mold and were washed out. Molds 4 and 5 were poured after introducing the alumina fibers into the remainder of the melt. The fibers were introduced in aluminum foil and plunged under the metal surface; power was applied to superheat the metal which was then poured. No fibers were observed in castings 4 and 5 using metallographic examination.

Heat 2. Four (4) pounds of alloy 36 were brought to a rolling melt in the induction unit. The tip of a graphite degassing rod was filled with fibers and plunged into the melt. Argon was blown through the tube to force the fibers into the melt. However, no fibers were evident in the castings poured in this manner.

Heat 3. Five (5) pounds of alloy 36 were induction melted and poured into button molds. Mold 1 contained fibers wrapped in aluminum foil. The stream of metal forced the fiber packet out of the mold. Mold 2 was filled and the fibers were plunged under the metal surface in the mold. Mold 3 was filled with metal and the fibers wrapped in Al foil were plunged under the metal surface then introduced into the remaining melt by plunging them below the surface and stirring. Molds 4, 5, 6 and 7 were then poured. Metallographic examination revealed no fibers in the cast structure of any of the samples poured with this heat.

Heat 4. Five (5) pounds of alloy 36 were melted and poured into seven button molds. Because of the difficulties encountered with previous mold design, a groove was incorporated into the edge of the molds to facilitate plunging the fibers into the metal. Seven molds were poured with the following fiber containing aluminum packets forced into the metal after pouring: 1 alumina, 2 aluminum nitride-oxide fiber crystals, 3 aluminum nitride-oxide

fiber crystals, 4 alumina, 5 aluminum nitride-oxide fiber crystals, 6 silicon carbide and 7 alumina. Metallographic examination revealed no fibers.

Heat 5. Five(5) pounds of alloy 36 were melted and poured into 5 button molds. Mold 1 was filled and the fibers wrapped in aluminum foil were plunged. Fibers wrapped in copper foil were then added to the melt and molds 2 and 3 were filled. Additional fibers wrapped in aluminum foil were added to the melt and molds 4 and 5 were filled. Metallographic examination revealed no fibers.

Although techniques similar to those described had been successfully employed for introducing and distributing fibers in aluminum and other alloys, the initial results of the experiments performed indicated that the high density and high melting point of Haynes alloy 36 were not compatible with the fiber introduction techniques previously utilized or attempted.

The experimental technique was scaled down to melting small quantities of metal with a TIG torch in a small graphite mold made by drilling a hole in a graphite plate. Some carbon was picked up by the metal but this was not deleterious with respect to the purpose of the experiments. To prevent the metal from being heated directly by the arc, the arc was struck between the electrode and graphite. This also reduced the turbulence which would be caused by the impinging gas. A variety of metals and techniques were attempted to introduce fibers into a metal or alloy which could then be introduced into the Haynes alloy 36 with no deterious effects on a large melt. The following melts were made by placing the fibers wrapped in aluminum foil at the bottom of the mold, covering the fibers with metal and melting.

Heat 1a*- Haynes alloy 36 - alumina fibers

Heat 2a - Haynes alloy 36 - silicon carbide fibers

Heat 3a - pure cobalt (99%) - alumina fibers

Heat 4a - pure nickel - alumina fibers

Heat 5a - 90% cobalt - 10% nickel - alumina fibers

Heat 6a - 90% cobalt - 10% nickel - silicon carbide fibers

Metallographic examination revealed no fibers in these samples.

Heat 7a - 90% cobalt - 10% nickel - alumina fibers

Fibers wrapped in aluminum foil were placed at the bottom of the crucible, covered by the metal, and then melted with a TIG torch. Borax was then added to the top of the melt and additional alumina fibers were then added through the borax. Some fibers were observed at the top of the solidified specimen. These fibers were most likely those inserted through the flux.

Heat 6. Four (4) pounds of Haynes alloy 36 were melted in an induction furnace. Premixed borax flux and alumina fibers were added to the melt after the power was shut-off. The melt rejected the flux, blowing it up and out of the crucible. Four specimens were poured. Metallographic examination revealed no fibers.

Heat 8a - Haynes alloy 36 - silicon carbide fibers

The metal was melted and an aluminum foil packet containing borax and fibers was added to the melt. Metallographic examination revealed no fibers.

Heat 9a - Haynes alloy 36 - silicon carbide fibers

The fibers were coated with boric acid and placed in the crucible with the charge. Metallographic examination revealed no fibers.

* Indicates small melt of approximately 20 grams.

Heat 7. A small graphite mold was filled with melted borax. Silicon carbide fibers were added to the molten borax. The solidified borax was then wrapped in aluminum foil. Four pounds of alloy 36 were melted and the prepared fibers plunged into the melt and stirred. Samples were then poured. Metallographic examination revealed no fibers.

Heat 8. Holes were drilled in 2 small pieces of Haynes alloy 36. Melted borax and fibers were then placed in the holes. Five pounds of Haynes alloy 36 were induction melted and the fibers added to the melt in the drilled samples. Metallographic examination of the test castings revealed no fibers.

Heat 10a - pure nickel - alumina fibers

The fibers were distributed in molten borax which was then added to the molten nickel. Metallographic examination revealed no fibers.

Heat 9. Five (5) pounds of alloy 36 were induction melted and poured into a tapered rectangular mold. Silicon carbide fibers were distributed on the drag portion of the mold. The fibers were washed to the end of the mold and were not picked up by the molten metal.

Heat 11a - Haynes alloy 36 - alumina fibers

Alumina fibers were placed in a hole drilled in a piece of alloy 36. The hole was plugged and the sample melted. No fibers were evident.

A series of experiments was then performed by melting alloy 36 in a resistance furnance using a graphite crucible. Although the small samples picked up a good deal of carbon, the object of the experiments was to introduce fibers into a small quantity of metal which could then be introduced

into a large melt.

Heat 12a - Haynes alloy 36 - silicon carbide and alumina fibers and borax were placed in the graphite mold and melted. Metallographic examination revealed alumina fibers distributed in the sample.

Heat 13a - Same as 12a with the exception that the molten metal was stirred and then allowed to cool. Metallographic examination revealed alumina fibers distributed in the sample.

Heat 10 - Five (5) pounds of alloy 36 were melted with borax and fibers distributed throughout the charge. The melt was cast into a cylindrical graphite mold. Metallographic examination revealed no fibers.

Heat 14a - Haynes alloy 36 - silicon carbide and alumina fibers and flux were melted and allowed to cool in a graphite mold. Metallographic examination revealed alumina fibers distributed in the sample.

Heat 15a - Haynes alloy 36 - silicon carbide and alumina fibers. Some fibers were placed in the bottom of the mold and covered with metal. When the metal was molten, additional fibers were added to the top of the melt and stirred in. Metallographic examination revealed alumina fibers distributed in the sample.

In order to definitely establish the presence of the alumina fibers in the carbon rich Haynes alloy 36, an electron micro-beam probe was run on sample 15a. The dark areas are definitely aluminum rich and since they fluoresced under the electron beam, it can be assumed it is an aluminum oxide phase. Figure 7 is sample 15a at low magnification showing the distribution of fibers in a matrix composed primarily of carbides. A variety of fiber sizes are evident. Figure 8 is the same sample at higher magnification illustrating the fibers which were determined to be alumina.

Figure 7 - Alumina Fibers Distributed in a Carbon Rich
Haynes Alloy 36

Electrolytic Etch 100X

Figure 8 - Alumina Fibers Distributed in a Carbon Rich

Haynes Alloy 36

Electrolytic Etch 500X

Heat 11 - Five (5) pounds of alloy 36 were induction melted. A small graphite crucible containing alumina and silicon carbide was dipped into the melt and filled with molten metal and allowed to solidify in the graphite crucible. Metallographic examination revealed no fibers.

Heat 12 - Same type of experiment as Heat 11 but the graphite crucible was replaced by an alundum crucible. The alundum crucible cracked and the experiment was scrapped.

Heat 13 - Five (5) pounds of alloy 36 were induction melted with SiC fibers placed in the crucible with the charge. SiC fibers wrapped in aluminum foil were plunged into the molten metal and fibers were also sprinkled on the surface of the melt and stirred in. Metallographic examination revealed no fibers in the cast sample.

Heat 14 - Five (5) pounds of alloy 36 were induction melted and a boron nitride crucible containing alumina and silicon carbide fibers was dipped into the melt and filled with molten metal. This was cast into a small mold. Metallographic examination revealed no fibers.

Heat 15 - Same procedure at Heat 14 with the addition of a flux to the fibers. Metallographic examination revealed no fibers.

Heat 16 - Same procedure as Heat 14 with the addition of borax. Metallographic examination revealed no fibers.

Heat 17 - Haynes alloy 36 was induction melted and three test bars were poured into a cylindrical test bar mold. A graphite crucible was used to ladle out the molten metal for the test bars. A control sample was cast. The ladle was again filled and 0.2g of silicon carbide and 0.2g of alumina fibers were plunged into the melt. After pouring the sample, some fibers were noticed on the crucible wall. The ladle was filled again and the same procedure was

used for the third sample. No fibers were observed in the ladle after pouring this sample. As a result, no definite numerical quantity of fibers can be associated with the samples, although there is a definite difference in the quantity of fibers in these two samples.

Heat 18 - Five (5) pounds of Haynes alloy 36 were induction melted and two control bars were cast. The melt was replenished and 1g. of alumina and 3g. of silicon carbide fibers were added to the melt and stirred in. Four test bars were poured.

Table I lists the samples poured and the results of the 1500°F short time tensile tests. The results will be discussed in the next section.

TABLE II

AS-CAST TENSILE PROPERTIES OF FIBER REINFORCED HAYNES ALLOY 36

TESTED AT 1500°F

Sample	Remarks	UTS	%E
17-3	Control	18,000 psi	0
17-1	< 0.1 wgt% Fibers	30,000	.8
17-2	> 0.1 wgt% Fibers	41,300	0
18-1	Control	18,080	1.5
18-2	Control	11,060	1.5
18-3	Porous		
18-4	Porous		
18-5	Fibers	31,870	.8
18-6	Porous		

III. DISCUSSION OF RESULTS

1) Based upon the results of extensive metallographic examination, it appears that the bulk of the alumina and silicon carbide fibers introduced into the Haynes alloy 36 are being dissolved by the matrix with one exception.

2) Fibers were observed in Haynes alloy 36 which had an increased carbon content. The increased carbon content was caused by melting Haynes alloy 36 in a graphite crucible, and a series of samples melted in this manner all contained alumina fibers. The fibers do not appear in a completely fibrous form in all cases but this can be attributed to the introduction of the fibers in small bundles which are not completely dispersed in the melt. The bundles appear to be the origin, in many cases, of a group of fibers extending into the solidified matrix. The increased carbon content appears to be contributing to the protection of the fibers in the molten matrix, and in many cases, the fibers appear at the center of the large carbides indicating the fibers are most likely serving as nuclei for the carbides.

The tensile properties of the fiber reinforced test bars pulled at 1500°F are not conclusive. Metallographic examination of the samples in the areas adjacent to the fracture surface indicated that no fibers were present. The tensile properties of samples poured from Heat 17 indicate a large improvement from the 18,000 psi UTS of the control to the 30,000 and 41,300 psi UTS of the samples containing fibers. Although higher strengths were achieved, in all cases the samples were extremely brittle, and the actual strengthening can be attributed to several other possible effects. The fibers which are dissolved or broken up in the molten matrix could be acting as dispersoids contributing

to high temperature strength. The graphite ladle and stirring rod used for this group of samples caused a gradual increase in carbon content. This would affect the mechanical properties. As the samples were poured, the melt temperature decreased and this would also affect the mechanical properties. The test samples poured from Heat 18 were generally porous and no conclusive results could be obtained.

Although fibers were distributed in small melts of Haynes alloy 36 with an increased carbon content, no successful fiber reinforced samples were produced with the scaled up techniques.

IV. CONCLUSIONS

It can be concluded from the extensive metallographic examination of samples in which the fibers were exposed to the molten matrix, that alumina and silicon carbide fibers are definitely attacked by the molten matrix in low carbon Haynes alloy 36.

Alumina fibers have been observed in Haynes alloy 36 which has been melted in graphite crucibles, which has the effect of increasing the carbon content of the alloy. The increased carbon content appears to be contributing to the protection of the fibers from attack by the molten matrix.

Although alumina fibers can be introduced into carbon saturated Haynes alloy 36, commercial use of such an alloy-fiber composite is not practical, because of the low ductility caused by the increased carbon content.

Though carbon saturated Haynes alloy 36 exhibits low tensile properties at 1500°F, the strength of this unsatisfactory material definitely increases substantially with increasing additions of alumina or silicon carbide fibers. The fibers seemed to act as dispersoids in the Haynes alloy 36 which freezes at essentially a single temperature. Previous work on aluminum alloys has shown that fibers will be found at grain boundaries in the alloys that freeze over a range of temperatures such as aluminum -4.5% copper alloy. This comes about because the fibers do not act as nuclei for precipitation, but are rejected into the last bit of liquid to solidify, which would be the material at or around the grain boundaries in the solidified composite. Based on the fact that the strength of carbon rich Haynes alloy 36 was affected drastically with small additions of fibers, it is reasonable to suggest that the same trend would be apparent in other cobalt base alloys which freeze

over a range of temperatures. Carbon rich alloys of this type containing fibers definitely located at grain boundaries would show a significant improvement in strength at elevated temperatures. Therefore, it is recommended that to further study the effect of ceramic fiber additions to cast cobalt base alloys, the limited research effort be continued to develop techniques for incorporating alumina and silicon carbide fibers into cobalt base alloys such as Haynes alloy 25 or Haynes Stellite 31 which freeze over a range of temperatures.

From the results obtained with the high carbon Haynes alloy 36, it appears that the carbon has a beneficial effect. If the alumina or silicon carbide fibers could be treated with a graphite coating instead of saturating the alloy melt with carbon, this might result in the formation of a carbide interface which protects the fiber without drastically increasing the carbon content of the alloy. Thus, the negative effect of the increased carbon content on ductility of the matrix would be eliminated while maintaining the protective mechanism necessary for the fibers. Therefore, the alloys previously mentioned which freeze over a range of temperature should be investigated in conjunction with graphite coated fibers.